

Thermal Conductivity Models for Carbon/Liquid Crystal Polymer Composites

Jason M. Keith, Julia A. King, Kara M. Lenhart, Bridget Zimny

Department of Chemical Engineering, Michigan Technological University, Houghton, Michigan 49931-1295

Received 2 December 2006; accepted 9 April 2007

DOI 10.1002/app.26607

Published online 24 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Thermally conductive resins are needed for bipolar plates in fuel cells. Currently, the materials used for these bipolar plates often contain a single type of graphite in a thermosetting resin. In this study, varying amounts of four different types of polyacrylonitrile carbon fillers (Ketjenblack carbon black, Thermocarb synthetic graphite, Fortafil 243 carbon fiber, and Panex 30 carbon fiber) were added to a thermoplastic matrix (Vectra A950RX Liquid Crystal Polymer), with the resulting resins tested for through-plane and in-plane thermal conductivity. There are two unique contributions of this work. The first contribution is the use of the Nielsen model for the through-plane thermal conductivity as

a function of the single filler volume fraction. The model fits the data for all composites well. The second contribution is the development of a new, accurate, empirical model to predict the in-plane thermal conductivity for all resins containing synthetic graphite or carbon fiber. Both of these models will form the basis for the development of new thermal conductivity models for composites with multiple fillers for fuel cell bipolar plate applications. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3309–3316, 2007

Key words: composites; fillers; liquid-crystalline polymers (LCP); thermal properties; modeling

INTRODUCTION

Most polymer resins are thermally insulating. Increasing the thermal conductivity of these resins allows them to be used in other applications. One emerging market for thermally conductive resins is for bipolar plates for use in fuel cells. The bipolar plate separates one cell from the next, with the plate carrying hydrogen gas on one side and air (oxygen) on the other side. Bipolar plates require high thermal conductivity (to conduct heat), low gas permeability, and good dimensional stability.

Typical thermal conductivity values for some common materials are 0.2–0.3 for polymers, 234 for aluminum, 400 for copper, and 600 for graphite (all values in $\text{W m}^{-1} \text{K}^{-1}$). One approach to improve the thermal conductivity of a polymer is through the addition of a conductive filler material such as carbon and metal. Conductive resins with a thermal conductivity from ~ 1 to $30 \text{ W m}^{-1} \text{K}^{-1}$ can be used in heat sink applications.¹

A significant amount of work has been conducted varying the amount of single conductive fillers in a composite material.^{2–9} For example, ceramic fibers/particles (boron nitride, aluminum nitride, aluminum oxide), metal fibers/particles (aluminum, steel, iron, copper, silver), and Ni-coated glass fibers have been used.^{3,10–13} Metallic fillers have several disadvantages, relative to carbon, which include higher density and greater susceptibility to oxidation. Various types of carbons have been effective conductive fillers. For example, synthetic graphite particles and carbon fibers are often added to polymers to increase the composite thermal conductivity.^{7,9,10,14,15}

In this project, researchers performed compounding runs followed by injection molding of carbon fiber/liquid crystal polymer (LCP) test specimens. Varying amounts of four different types of carbon fillers (Ketjenblack carbon black, Thermocarb synthetic graphite, Fortafil 243 carbon fiber, and Panex 30 carbon fiber) were added to Vectra A950RX LCP. The resulting single filler composites were then tested for thermal conductivity.

We note that a long term goal of this research project is to understand the effects of multiple carbon fillers on the thermal properties of fuel cell bipolar plates. Fundamental research is required to attain this goal, namely the experimental measurement and model formulation for the single filler composites, with regard to in-plane and through-plane thermal conductivities. These results are presented here. For experimental testing, we use the guarded heat flow

Correspondence to: J. M. Keith (jmkeith@mtu.edu).

Contract grant sponsor: Department of Energy; contract grant number: DE-FG02-04ER63821.

Contract grant sponsor: National Science Foundation; contract grant number: DMI-0456537.

Contract grant sponsor: Michigan Space Grant Consortium.

Journal of Applied Polymer Science, Vol. 105, 3309–3316 (2007)
© 2007 Wiley Periodicals, Inc.

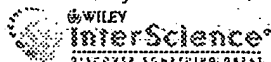


TABLE I
Properties of Ticona's Vectra A950RX³⁴

Melting point	280°C
Tensile modulus (1 mm/min)	10.6 GPa
Tensile stress at break (5 mm/min)	182 MPa
Tensile strain at break (5 mm/min)	3.4%
Flexural modulus at 23°C	9.1 GPa
Notched izod impact strength at 23°C	95 kJ/m ²
Density at 23°C	1.40 g/cm ³
Volumetric electrical conductivity at 23°C	10 ⁻¹⁵ S/cm
Surface electrical conductivity	10 ⁻¹⁴ S
Thermal conductivity at 23°C	0.2 W m ⁻¹ K ⁻¹ (approx.)
Humidity absorption (23°C/50% RH)	0.03 wt %
Mold shrinkage-parallel	0.0%
Mold shrinkage-normal	0.7%
Coefficient of linear thermal expansion-parallel	0.04 × 10 ⁻⁴ /°C
Coefficient of linear thermal expansion-normal	0.38 × 10 ⁻⁴ /°C

method to measure through-plane thermal conductivity¹⁶ and the transient plane source method,¹⁷⁻²¹ a relatively new analytical technique, which allows for measurement of both the in-plane and through-plane thermal conductivities in a single experiment.

There are two specific modeling-related goals of this research, which are new contributions to the composites literature. The first goal was to apply Nielsen's thermal conductivity model²² for the through-plane thermal conductivity of these formulations. The second goal is to use a simple empirical model developed earlier in our group,^{23,24} along with the Nielsen model results, to predict in-plane thermal conductivities. We note that the technical literature has extensive experimental and modeling data for through-plane thermal conductivity,^{22,25-33} but there is little reported experimental data nor model development for the in-plane thermal conductivity.

MATERIALS AND EXPERIMENTAL METHODS

Materials

The matrix used for this project was Ticona's (Summit, NJ) Vectra A950RX LCP, which is a highly ordered thermoplastic copolymer consisting of 73 mol % hydroxybenzoic acid and 27 mol % hydroxynaphtholic acid. This LCP has the properties needed for bipolar plates, namely high-dimensional stability up to a temperature of 250°C, extremely short molding times (often 5–10 s), exceptional dimensional reproducibility, chemically resistant in acidic environments present in a fuel cell, and a low hydrogen

gas permeation rate.^{34,35} The properties of this polymer are shown in Table I.³⁴

The first carbon filler used in this study was Ketjenblack EC-600 JD, carbon black. This is an electrically conductive carbon black available from Akzo Nobel (Chicago, IL). The highly branched, high surface area carbon black structure allows it to contact a large amount of polymer, which results in improved electrical conductivity at low carbon black concentrations (often 5–7 wt %). The properties of carbon black are given in Table II.³⁶ According to the vendor literature, carbon black is sold in the form of pellets that are 100 µm–2 mm in size and, upon mixing into a polymer, easily separates into primary aggregates 30–100-nm long.³⁶ A diagram of the carbon black structure is shown in vendor literature³⁶ and prior work from our group.³⁷ It is noted that the thermal conductivity of pure carbon black cannot be estimated because of the small size of the aggregates.

Table III shows the properties of the Asbury Carbons' (Asbury, NJ) Thermocarb TC-300, which is a primary synthetic graphite that was previously sold by Conoco (Houston, TX).^{38,39} Thermocarb TC-300 has high electrical and thermal conductivity, and a mean particle aspect ratio of ~ 1.7. Thermocarb TC-300 is produced from a thermally treated, highly aromatic petroleum feedstock, and contains very few impurities. A photomicrograph of this synthetic graphite is shown in the vendor literature³⁸ and prior work from our group.³⁷

Fortafil 243, sold by Toho Tenax America (Rockwood, NJ) is a polyacrylonitrile (PAN)-based 3.2-mm chopped and pelletized carbon fiber used to improve the electrical and thermal conductivity of the resin. Fortafil 243 was surface-treated and then formed into pellets. A proprietary polymer (sizing) is used as a binder for the pellets that also promotes adhesion with the matrix. Table IV shows the properties of this carbon fiber, which is 95 wt % carbon.⁴⁰

Table V shows the properties of Zoltek's (St. Louis, MO) Panex 30 MF milled 150-µm long high purity carbon fiber. This carbon fiber is PAN-based and is electrochemically surface-treated but not sized. Panex 30 is produced by a high-temperature

TABLE II
Properties of Akzo Nobel Ketjenblack EC 600-JD
Carbon Black³⁶

Electrical resistivity	0.01–0.1 Ω cm
Aggregate size	30–100 nm
Specific gravity	1.8 g/cm ³
Apparent bulk density	100–120 kg/m ³
Ash content, max	0.1 wt %
Moisture, max	0.5 wt %
Brunauer–Emmett–Teller surface area	1250 m ² /g
Pore volume	480–510 cm ³ /100 g

TABLE III
Properties of Thermocarb TC-300 Synthetic Graphite^{38,39}

Filler	Thermocarb TC-300 synthetic graphite
Carbon content (wt %)	99.91
Ash (wt %)	<0.1
Sulfur (wt %)	0.004
Density (g/cm ³)	2.24
Brunauer-Emmett-Teller surface area (m ² /g)	1.4
Thermal conductivity at 23°C (W m ⁻¹ K ⁻¹)	600 in. "a" crystallographic direction
Electrical conductivity of bulk carbon powder at 150 ψ , 23°C, parallel to pressing axis (S/cm)	50
Particle shape	Acicular
Particle aspect ratio	1.7
Sieve analysis, microns (wt %)	
+600 μ m	0.19
+500 μ m	0.36
+300 μ m	5.24
+212 μ m	12.04
+180 μ m	8.25
+150 μ m	12.44
+75 μ m	34.89
+44 μ m	16.17
-44 μ m	10.42

batch graphitization process that produces fiber that is 99.5 wt % carbon.⁴¹ Panex 30 also has a high electrical and thermal conductivity.

Thermal conductivity was measured on composites containing varying amounts of these carbon fibers in Vectra A950RX. The concentrations (shown in wt % and the corresponding vol %) for these single filler composites are shown in Table VI.

Test specimen fabrication

For this entire project, the fillers were used as-received. Vectra A950RX was dried in an indirect-heated dehumidifying drying oven at 150°C and then stored in moisture barrier bags.

TABLE IV
Properties of Fortafil 243 Carbon Fiber⁴⁰

Carbon content	95 wt %
Electrical resistivity	0.00167 Ω cm
Thermal conductivity	20 W m ⁻¹ K ⁻¹ (axial direction)
Tensile strength	3800 MPa
Tensile modulus	227 GPa
Specific gravity	1.74 g/cm ³
Fiber diameter	7.3 μ m
Fiber shape	Round
Fiber mean length	3.2 mm (entire range is 2.3–4.1 mm)
Binder content	2.6 wt % proprietary polymer that adheres pellet together and promotes adhesion with nylon matrix
Bulk density	356 g/L

TABLE V
Properties of Panex 30 MF Milled High Purity Carbon Fiber⁴¹

Carbon content	99.5 wt %
Electrical resistivity	0.0014 Ω cm
Thermal conductivity	22 W m ⁻¹ K ⁻¹ (axial direction, approximate)
Tensile strength	3600 MPa
Tensile modulus	207 GPa
Specific gravity	1.75 g/cm ³
Fiber diameter	7.4 μ m
Fiber shape	Round
Fiber mean length	150 μ m
Bulk density	445 g/L

The extruder used was an American Leistritz Extruder Corp. (Somerville, NJ) model ZSE 27. This extruder has a 27-mm corotating intermeshing twin screw with 10 zones and a length/diameter ratio of 40. The screw design used is the same as that used in prior published research.⁴² The screw design was chosen to allow a large concentration of filler to mix with the matrix material and thereby achieve the maximum possible conductivity. The Vectra polymer pellets were introduced in Zone 1. A side stuffer located at Zone 5 was used to introduce the carbon fillers into the polymer melt. Two Schenck (White-water, WI) AccuRate gravimetric feeders were used to accurately control the amount of each material added to the extruder.

After passing through the extruder, the composite strands (3 mm in diameter) entered a water bath and then a pelletizer that produced nominally 3-mm long pellets. After compounding, the pelletized com-

TABLE VI
Single Filler Loading Levels in Vectra A950RX

Filler (wt %)	Carbon black (vol %)	Thermocarb TC-300 (vol %)	Fortafil 243 (vol %)	Panex 30 (vol %)
2.5	1.9	N/A	N/A	N/A
4.0	3.1	N/A	N/A	N/A
5.0	3.9	N/A	4.1	4.0
6.0	4.7	N/A	N/A	N/A
7.5	6.0	N/A	6.1	6.1
10	8.0	6.5	8.2	8.2
15	12.1	9.9	12.4	12.4
20	N/A	13.5	16.8	16.7
25	N/A	17.2	21.2	21.1
30	N/A	21.1	25.5	25.5
35	N/A	25.2	30.2	30.1
40	N/A	29.3	34.9	34.8
45	N/A	33.8	39.7	39.9
50	N/A	38.5	44.6	44.4
55	N/A	43.3	49.6	49.4
60	N/A	48.4	54.7	54.5
65	N/A	53.7	N/A	N/A
70	N/A	59.3	N/A	N/A
75	N/A	65.2	N/A	N/A

posite resin was dried again and then stored in moisture barrier bags prior to injection molding.

A Niigata (Itasca, IL) injection molding machine, model NE85UA₄, was used to produce test specimens. This machine has a 40-mm diameter single screw with a length/diameter ratio of 18. The lengths of the feed, compression, and metering sections of the single screw are 396, 180, and 144 mm, respectively. A four-cavity mold was used to produce 6.4-cm diameter (end gated) 3.2-mm thick disks. The thermal conductivity of all formulations was determined. Prior to conducting thermal conductivity tests, the samples were conditioned at 23°C and 50% relative humidity for 88 h and then tested.⁴³

Filler length and orientation test method

Because of the small size of the carbon black (the primary aggregates were 30–100 nm), the carbon black filler length and orientation were not measured. The following procedure was used to determine the length of the other carbon fillers in the molded test specimens.^{33,44} Diethylenetriamine was used to dissolve the matrix. The fillers were then dispersed onto a glass slide and viewed using an Olympus (Center Valley, PA) SZH10 reflected light microscope at a magnification of 60 \times . Digital images were taken of the filler and were then analyzed with Adobe (San Jose, CA) Photoshop version 5.0 installed with the Image Processing Toolkit.

The following procedure was used to determine the orientation of the synthetic graphite and carbon fibers.^{33,44} For the thermal conductivity samples, the center portion was cut out of a disk and set in epoxy such that the through sample thickness (3.2 mm) face could be viewed. The samples were then polished and viewed using an Olympus BX60 reflected light microscope at a magnification of 200 \times .

Through-plane thermal conductivity test method

The through-plane thermal conductivity of a 3.2-mm thick, 5-cm diameter disc-shaped test specimen was measured at 55°C using a Holometrix (Burlington, MA) Model TCA-300 Thermal Conductivity Analyzer according to the ASTM F433 guarded heat flow meter method.¹⁶ For each formulation, six samples were tested.

Transient plane source thermal conductivity test method

The Mathis Instruments (Halifax, Nova Scotia, Canada) Hot Disk Thermal Constants Analyzer is an emerging technology that can measure the in-plane and through-plane thermal conductivity of an anisotropic material in the same test, using the transient

plane source technique.^{17–24,45,46} The sensor used in this test method consisted of a 10- μ m thick nickel foil embedded between two 25.4- μ m-thick layers of Kapton polyimide film. The nickel foil was wound in a double spiral pattern with a radius R of 3.189 mm. This sensor is placed between two polymer composite disks of diameter $D = 63.5$ mm and thickness $T = 3.18$ mm. The thermal conductivities were measured at 23°C. During the experiment, the sensor was heated by a constant electrical current (about 0.05 W) over a short period of time (typically 5 s). The generated heat dissipated within the double spiral is conducted through the kapton insulating layer and into the surrounding sample, causing a rise in the temperature of the sensor and the sample. The average transient temperature increase of the sensor is simultaneously measured by recording the change in electrical resistance of the nickel sensor and can then be used to back-calculate the in-plane and through-plane thermal conductivities of the polymer composite.

RESULTS

Filler length and orientation results

For the molded test specimens containing synthetic graphite, the filler length and aspect ratio were typically 50 μ m and 1.68, respectively. The synthetic graphite length results are comparable to that of Heiser and King³³ For the molded test specimens containing both carbon fibers, the fiber length was typically 70 μ m. The corresponding fiber aspect ratio (length/diameter) was 9. The carbon fiber length results are comparable to that of Heiser and King³³ and Bigg.⁴⁷

As shown previously for the through-plane thermal conductivity samples, the fillers are primarily oriented transverse to the conductivity measurement direction. These results are comparable to our prior work on filler orientation.³³ Photomicrographs are available in the published literature.^{33,42}

Thermal conductivity experimental results

The filler size, shape, concentration, dispersion (degree of mixing), orientation, bonding between the filler and matrix, thermal conductivity of the constituents (filler and matrix), and the crystallinity of the polymer (increasing crystallinity improves thermal conductivity) are factors that affect the thermal conductivity of a composite. Figures 1 and 2 display the experimental through-plane thermal conductivity data k_{through} for the samples containing Ketjenblack, Thermocarb, Fortafil 243, and Panex 30. Several generalizations can be made regarding these data. First of all, it is noted that at higher loading levels, the Thermocarb composites exhibited the highest thermal conductivity of the filled

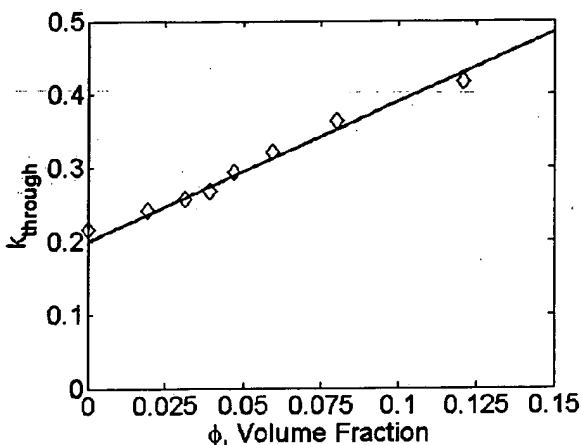


Figure 1 Through-plane experimental (data points) and theoretical (line) thermal conductivities in $\text{W m}^{-1} \text{K}^{-1}$ for composites containing Ketjenblack (diamonds).

composites tested. This can be attributed to the high thermal conductivity of the Thermocarb ($600 \text{ W m}^{-1} \text{K}^{-1}$) when compared with the carbon fibers (both about $20 \text{ W m}^{-1} \text{K}^{-1}$) and carbon black (thermal conductivity measurement was not available, but we estimate it as $2.1 \text{ W m}^{-1} \text{K}^{-1}$ in the modeling section of this article). Second, the Ketjenblack composites exhibit a relatively linear increase in through-plane thermal conductivity over the range of filler volume fractions tested in this research. We could not extrude or injection mold composites with filler loadings above 12.1 vol % due to the large increase in composite viscosity, as we note in a prior publication.⁴² We note that for the synthetic graphite or carbon fiber composites, the thermal conductivity is relatively linear for volume fractions less than 0.12, after which there is a rapid

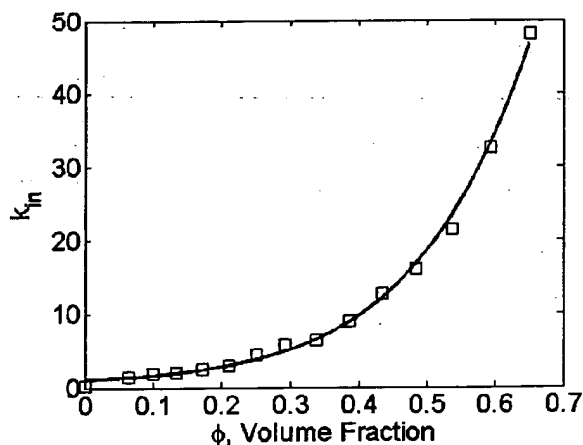


Figure 3 In-plane experimental (data points) and theoretical (line) thermal conductivities in $\text{W m}^{-1} \text{K}^{-1}$ for composites containing Thermocarb (squares).

growth. This rapid growth can likely be attributed to significant conductive pathways formed in the composite.

The in-plane thermal conductivities, k_{in} for Thermocarb, Fortafil 243, and Panex 30 are shown as a function of filler volume fraction ϕ in Figures 3 and 4. Composites containing Ketjenblack were not tested for in-plane thermal conductivity, as their thermal conductivity is too low for the test method considered here. Composites containing Thermocarb have higher in-plane thermal conductivities for all filler loading levels. It is noted that the Thermocarb/Vectra composites likely have higher in-plane thermal conductivity because of the higher thermal conductivity of the constituent Thermocarb ($600 \text{ W m}^{-1} \text{K}^{-1}$) compared with the Fortafil 243 and Panex 30 fibers (both about $20 \text{ W m}^{-1} \text{K}^{-1}$).

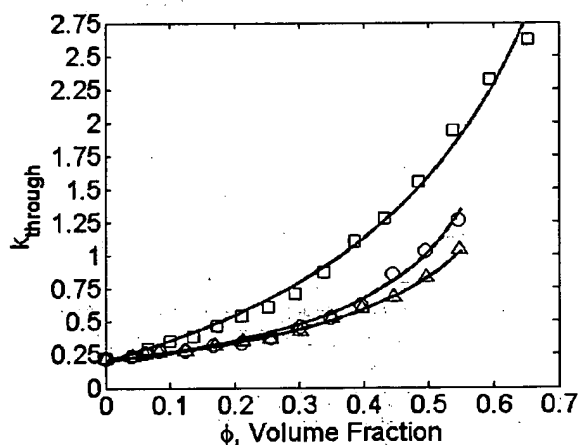


Figure 2 Through-plane experimental (data points) and theoretical (lines) thermal conductivities in $\text{W m}^{-1} \text{K}^{-1}$ for composites containing Thermocarb (squares), Fortafil 243 (triangles), and Panex 30 (circles).

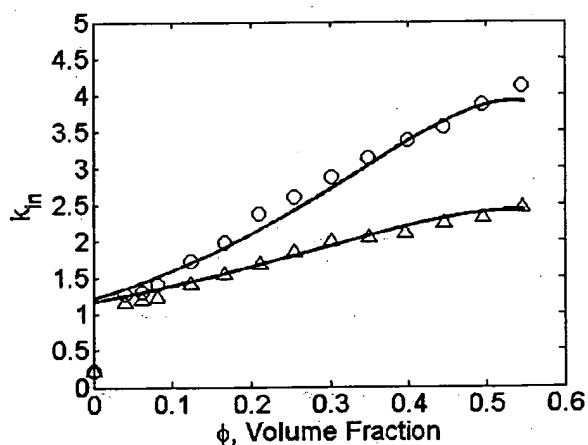


Figure 4 In-plane experimental (data points) and theoretical (line) thermal conductivities in $\text{W m}^{-1} \text{K}^{-1}$ for composites containing Fortafil 243 (triangles) and Panex 30 (circles).

Thermal conductivity modeling background

In many engineering applications, including that for bipolar plates in fuel cells, composite materials are thin with respect to one dimension. Many of the experimental techniques, and therefore development of thermal conductivity models, have been applied toward predicting the through-plane thermal conductivity of a composite. However, as new experimental techniques have been developed to measure the in-plane thermal conductivity,¹⁷⁻²¹ it is also desired to develop models for this transport property as well. After briefly reviewing the modeling literature, we describe our modeling approach for the anisotropic thermal conductivities of the composites tested here.

For simplicity as well as direct application to the research presented here, we will focus on a system with one filler. The following nomenclature will be used: K represents the thermal conductivity of the composite, k_i the thermal conductivity of the i th constituent (1 = matrix, 2 = filler), and ϕ the volume fraction of the filler (note $1 - \phi$ is the matrix volume fraction).

The most basic thermal-conductivity models are the standard rule of mixtures [eq. (1)], inverse rule of mixtures [eq. (2)], and the geometric rule of mixtures [eq. (3)].²⁸

$$K = (1 - \phi)k_1 + \phi k_2 \quad (1)$$

$$\frac{1}{K} = \frac{(1 - \phi)}{k_1} + \frac{\phi}{k_2} \quad (2)$$

$$K = k_1^{(1-\phi)} + k_2^\phi \quad (3)$$

It is noted that these models work well for continuous, periodic geometries, such as stratified slabs in a parallel (rule of mixtures) or transverse (inverse rule of mixtures) orientation with the direction of heat conduction. However, if the materials are not continuous, as is the case for carbon-filled resins, the models are not accurate.

There are many advanced models for composite systems. The basis of many of them is from Maxwell and is based upon potential theory to obtain an exact solution for the conductivity of a system with spherical noninteracting particles in a continuous matrix.²⁵ As most systems do not have noninteracting spherical particles, this model is restricted in its utility. Hamilton and Crosser²⁷ developed a semitheoretical model that can account for filler shape. The parameter ψ indicates the sphericity of the particles, typically between 0.58 and 1.0 for the investigated data sets. Their model is given as

$$K = k_1 \left(\frac{k_2 + (n-1)k_1 + (n-1)\phi(k_2 - k_1)}{k_2 + (n-1)k_1 - \phi(k_2 - k_1)} \right) \quad (4a)$$

$$n = \frac{3}{\psi} \quad (4b)$$

When $n = 3$, their model reduces to the Maxwell model. The Bruggeman²⁶ theoretical model also follows Maxwell's derivation, but with different assumptions about the permeability and field strength of the system. It is given as

$$1 - \phi = \frac{k_2 - K}{k_2 - k_1} \left(\frac{k_1}{K} \right)^{1/3} \quad (5)$$

Other advanced models can be derived from the hypothesis that the ratio of thermal conductivity of a composite material to that of the pure polymer is proportional to the increase in viscosity, tensile modulus, and/or shear modulus. The original basis for many of these models is Albert Einstein's model for the viscosity of a fluid with dispersed spheres. On the basis of this premise, McCullough and coworkers^{29,30} proposed a generalized equation in combination with traditional mixing rules and a reference state, used in composites that show orthotropic symmetry. The McCullough model, with some rearrangement, serves as the basis for the Halpin-Tsai equations²⁸:

$$\frac{K}{k_1} = \frac{1 + \xi\chi\phi}{1 - \chi\phi} \quad (6a)$$

$$\chi = \frac{k_2/k_1 - 1}{k_2/k_1 + \xi} \quad (6b)$$

where ξ varies depending upon the filler used. Lewis and Nielsen²² improved upon the Halpin-Tsai model by adding a value to the denominator of the primary equation, given by the symbol ψ to take into account the filler shape, orientation, and the packing. The model is given as

$$\frac{K}{k_1} = \frac{1 + AB\phi}{1 - B\psi\phi} \quad (7a)$$

$$B = \frac{k_2/k_1 - 1}{k_2/k_1 + A} \quad (7b)$$

$$\psi \cong 1 + \frac{1 - \phi_m}{\phi_m^2} \phi \quad (7c)$$

where ϕ_m term is the maximum volumetric packing fraction of the filler. The parameters A and ϕ_m has been tabulated for some filler types and orientation in the literature.¹³

Progelhof et al.²⁸ reviewed many composite thermal-conductivity models. This review determined that the Nielsen model fits the data the best over the given data range (0–30 vol %) for a two-phase system. This review studied 62–88- μm diameter glass spheres and 62–125- μm diameter magnesium oxide powder in polyethylene. Work done by Weber and colleagues^{31,32} has expanded the Nielsen model into a form more applicable for multiple-filler systems. The primary change in the system of equations occurs in eq. (7a), where the contributions from fillers are accounted for in a summation term.

Recently, with the advent of the transient plane source method, our group has been able to obtain in-plane and through-plane thermal conductivity data. An empirical correlation^{23,24} has been developed for the square root of the product of the in-plane and through-plane thermal conductivities given as

$$\sqrt{k_{\text{in}}k_{\text{through}}} = C e^{D\phi} \quad (8)$$

where C and D are adjustable parameters.

Through-plane thermal conductivity modeling results

In this section we use Nielsen's model to predict the through-plane thermal conductivity k_{through} of conductive resins in ($\text{W m}^{-1} \text{K}^{-1}$) as a function of the filler volume fraction ϕ . It is noted that Nielsen's model typically uses fixed data for the parameters A and ϕ_m , depending on the filler shape, aspect ratio, and packing. However, these models have been shown either to underestimate thermal conductivity or break down at higher filler concentrations.^{2,31,32,46,48} Thus, the theoretical through-plane thermal conductivities k_{through} for Thermocarb, Fortafil 243, and Panex were calculated using eq. (7) by adjusting the values of the shape factor A and maximum packing fraction ϕ_m . In all cases, $k_1 = 0.2 \text{ W m}^{-1} \text{K}^{-1}$ (Table II). The results are shown in Figure 2 with parameters given as follows:

Thermocarb: $k_2 = 600 \text{ W m}^{-1} \text{K}^{-1}$ (Table III), $A = 6.0$, $\phi_m = 1.00$

Fortafil 243: $k_2 = 20 \text{ W m}^{-1} \text{K}^{-1}$ (Table IV), $A = 1.7$, $\phi_m = 0.80$

Panex 30: $k_2 = 22 \text{ W m}^{-1} \text{K}^{-1}$ (Table V), $A = 2.0$, $\phi_m = 0.72$

We note that for carbon black the maximum volume fraction tested was low enough that the value of $\phi_m = 0.64$ used in previous work^{31,32} was not exceeded. However, the thermal conductivity of car-

bon black is variable, and was used here as an adjustable parameter along with the shape factor. The results of the model are shown in Figure 1 with the parameters given as

Carbon black: $k_2 = 2.1 \text{ W m}^{-1} \text{K}^{-1}$, $A = 1720$, $\phi_m = 0.64$

In-plane thermal conductivity modeling results

It was also desired as part of this work to develop a simple model for the in-plane thermal conductivity k_{in} by combining eqs. (7) and (8). We note that for Vectra/Thermocarb²³ composites (up to 65 vol %), $C = 0.4638 \text{ W m}^{-1} \text{K}^{-1}$ and $D = 4.9256$, for Vectra/Fortafil 243 carbon fiber²⁴ composites (up to 55 vol %), $C = 0.4841 \text{ W m}^{-1} \text{K}^{-1}$ and $D = 2.1478$, and for Vectra/Panex 30 carbon fiber²⁴ composites (up to 55 vol %), $C = 0.4927 \text{ W m}^{-1} \text{K}^{-1}$ and $D = 2.7933$. It is noted that in eq. (8) all thermal conductivities must have units of $\text{W m}^{-1} \text{K}^{-1}$. Based upon these results, a new model can be developed for the in-plane thermal conductivity:

$$k_{\text{in}} = \frac{C^2 e^{2D\phi}}{k_{\text{through}}} \quad (9)$$

with k_{through} given by K in eq. (7).

The results of this model are shown in Figures 3 and 4 and will now be discussed. There is a very good agreement between the model and the experimental data. It is noted that the models for the resins containing carbon fiber tend to level off as the volume fraction is increased, indicating a possible limiting value of k_{in} . Mathematically, this occurs because the rate of growth of k_{through} as predicted by eq. (7) exceeds that of the product $k_{\text{through}} k_{\text{in}}$ in eq. (8). This situation may be alleviated by choosing an alternate form of eq. (7c) for the through-plane thermal conductivity.

Equations (7) and (8) are empirical models based upon experimental results. However, there is currently limited through-plane experimental data available for polymer composite systems with high loading levels, and for in-plane experimental data at any loading level. A rigorous parametric study investigating various systems with differing filler orientation, length, aspect ratio, and thermal properties is required to obtain a better fundamental understanding of composite thermal conductivity and allow for development of more theoretically based models.

CONCLUSIONS

In this project, four different carbon fillers (Ketjen-black carbon black, Thermocarb synthetic graphite, Fortafil 243 carbon fiber, and Panex 30 carbon fiber)

were tested for thermal conductivity at single filler loadings of up to 75 wt % (65 vol %) in Vectra A950RX LCP. Through-plane and in-plane thermal conductivities were measured. When comparing the results of resins containing Thermocarb, Fortafil 243, or Panex 30, the Thermocarb composites exhibited higher through-plane and in-plane thermal conductivities over the entire range of fillers studied.

The Panex 30 composites also showed improved through-plane thermal conductivity when compared with Fortafil 243 composites at filler loadings above 40 vol %. At lower loadings, the through-plane thermal conductivities were identical. However, the Panex 30 composites always had higher in-plane thermal conductivity. These differences may be attributed to the slightly higher thermal conductivity of Panex 30 when compared with Fortafil 243 (Tables IV and V).

Two model results were presented here: the Nielsen model for the through-plane thermal conductivity and a new model for the in-plane thermal conductivity. This new model utilizes a previously developed correlation for the square root of the product of the in-plane and through-plane thermal conductivities $\sqrt{k_{in}k_{through}}$ and the Nielsen model. The results showed good agreement with the experimental data. In future research, these models will form the basis for the development of new thermal conductivity models for composites with multiple fillers.

The authors thank the American Leistritz technical staff for recommending an extruder screw design. The authors also acknowledge the following undergraduate students for their assistance on this project: Terrence Mazure, Stephanie Natrass, Troy Tambling, Elaine Venema, and Amanda Zalud.

References

- Finan, J. M. In *Proceedings of the Society of Plastics Engineers Annual Technical Conference*, 1999; p 1547.
- Agari Y.; Uno, T. *J Appl Polym Sci* 1985, 30, 2225.
- Bigg, D. M. *Polym Eng Sci* 1977, 17, 842.
- Bigg, D. M. *Adv Polym Technol* 1984, 4, 255.
- Narkis, M.; Lidor, G.; Vaxman, A.; Zuri, L. *J Electrostat* 1999, 47, 201.
- Nagata, K.; Iwabuki, H.; Nigo, H. *Compos Interfaces* 1999, 6, 483.
- Demain, A. Ph.D. Dissertation, Universite Catholique de Louvain, Louvain-la-Neuve, Belgium, 1994.
- King, J. A.; Tucker, K. W.; Meyers, J. D.; Weber, E. H.; Clingerman, M. L.; Ambrosius, K. R. *Polym Compos* 2001, 22, 142.
- Murthy, M. V. In *Proceedings of the Society of Plastics Engineers Annual Technical Conference*, 1994; p 1396.
- Taipalus, R.; Harmia, T.; Zhang, M. Q.; Friedrich, K. *Compos Sci Technol* 2001, 61, 801.
- Simon, R. M. *Polym News* 1985, 11, 102.
- Mapleston, P. *Mod Plast* 1992, 69, 80.
- Bigg, D. M. *Polym Compos* 1986, 7, 125.
- Brosius, B. *High Perform Compos* 2001, September/October, 22.
- Thongruang, W.; Spontak, B. J.; Balik, C. M. *Polymer* 2002, 43, 3717.
- American Society for Testing and Materials (ASTM). *Standard test methods for evaluating thermal conductivity of gasket materials*, ASTM Standard F433-77 (Reapproved 1993), ASTM: Philadelphia, 1998.
- Gustavsson, M.; Karawacki, E.; Gustafsson, S. E. *Rev Sci Instrum* 1994, 65, 3856.
- Log, T.; Gustafsson, S. E. *Fire Mater* 1995, 19, 43.
- Bohac, V.; Gustavsson, M. K.; Kubicar, L.; Gustafsson, S. E. *Rev Sci Instrum* 2000, 71, 2452.
- Hot disk thermal constants analyzer instruction manual, Mathis Instruments, Ltd.: Fredericton, New Brunswick, Canada, 2001.
- Transient plane source- gustafsson hot disk technique, standards for contact transient measurements of thermal properties. National Physical Laboratory: United Kingdom. Available at <http://www.npl.co.uk/thermal/ctm>. Last accessed November 2006.
- Nielsen, L. *Ind Eng Chem Fundam* 1974, 13, 17.
- Miller, M. G.; Keith, J. M.; King, J. A.; Edwards, B. J.; Klinkenberg, N.; Schiraldi, D. A. *Polym Compos* 2006, 27, 388.
- Keith, J. M.; King, J. A.; Miller, M. G.; Tomson, A. M. *J Appl Polym Sci* 2006, 102, 5456.
- Maxwell, J. C. *A Treatise on Electricity and Magnetism*, 3rd ed.; Dover: New York, 1954; Chapter 9, p 1.
- Bruggeman, D. *Ann Phys* 1935, 24, 636.
- Hamilton, R. L.; Crosser, O. *Ind Eng Chem Fund* 1962, 1, 187.
- Progelhof, R. C.; Throne, J. L.; Reutsch, R. R. *Polym Eng Sci* 1976, 16, 615.
- McGee, S.; McCullough, R. L. *Polym Compos* 1981, 2, 149.
- McCullough, R. *Compos Sci Technol* 1985, 22, 3.
- Weber, E. H. Ph.D. Dissertation, Michigan Technological University, Houghton, MI, 2001.
- Weber, E. H.; Clingerman, M. L.; King, J. A. *J Appl Polym Sci* 2003, 88, 123.
- Heiser, J. A.; King, J. A. *Polym Compos* 2004, 25, 186.
- Ticona Vectra Liquid Crystal Polymer (LCP) Product Information; Ticona: Summit, NJ, 2000.
- Chiou, J. S.; Paul, D. R. *J Polym Sci Part B: Polym Phys* 1987, 25, 1699.
- Akzo Nobel Electrically Conductive Ketjenblack Product Literature; Akzo Nobel: Chicago, IL, 1999.
- Keith, J. M.; King, J. A.; Barton, R. L. *J Appl Polym Sci* 2006, 102, 3293.
- Asbury Carbons Product Information; Asbury: NJ, 2004.
- Conoco Carbons Products Literature; Conoco: Houston, TX, 1999.
- Toho Tenax America, Inc. Fortafil Carbon Fibers technical Data Sheet; Toho Tenax America: Rockwood, TN.
- Zoltek Panex Carbon Fibers Technical Data Sheet; Zoltek Panex: St Louis, MO, 2005.
- King, J. A.; Morrison, F. A.; Keith, J. M.; Miller, M. G.; Smith, R. C.; Cruz, M.; Neuhalfen, A. M.; Barton, R. L. *J Appl Polym Sci* 2006, 101, 2680.
- International Standard Organization (ISO). *Plastics- Standard Atmospheres for Conditioning and Testing*, ISO 291:1997; ISO: Switzerland, 1998.
- Heiser, J. A.; King, J. A.; Konell, J. P.; Sutter, L. L. *Polym Compos* 2004, 25, 407.
- He, Y. *Thermochim Acta* 2005, 436, 122.
- Keith, J. M.; Hingst, C. D.; Miller, M. G.; King, J. A.; Häuser, R. A. *Polym Compos* 2006, 27, 1.
- Bigg, D. M. *Polym Compos* 1985, 6, 20.
- King, J. A.; Tucker, K. W.; Vogt, B. D.; Weber, E. H.; Quan, C. *Polym Compos* 1999, 20, 643.